Dielectric Behavior of Water Molecules Adsorbed on Iron(III) Oxide Hydroxides

Katsumi Kaneko, Mamoru Serizawa, Tatsuo Ishikawa, and Katsuya Inouye
Department of Chemistry, Faculty of Science, Chiba University, Yayoi-cho, Chiba 280

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The change in the dielectric constant of α-FeOOH, β-FeOOH, and γ-FeOOH with the amount of adsorbed water was examined at 30.0 °C in the frequency range 200 Hz—100 kHz for the purpose of clarifying the mechanism of water adsorption. The adsorption isotherms belong to the BET II type. The sample with the adsorbed water shows a particular dispersion of the dielectric constant with frequency in the low frequency range. The dispersion was ascribed to the transition between different orientational directions of the dipole moment of the adsorbed water. The change in the dielectric constant with the amount of adsorbed water for each iron(III) oxide hydroxide was interpreted in relation to the surface structure of predominant faces of crystals, in particular the number and position of hydroxyls on crystal surfaces. The following adsorption process was suggested below the monolayer adsorption coverage for each iron(III) oxide hydroxide. For α-FeOOH, water molecules are adsorbed on the (100) planes in three successive steps. For β-FeOOH, water molecules are primarily bound in the tunnels existing in the crystal along a direction parallel to the c-axis and then are adsorbed on the cracked tunnels exposing to the outer surface. For γ-FeOOH, water molecules are adsorbed on the (010) planes in two steps.

Of the four polymorphs of iron(III) oxide hydroxide (the so-called ferric oxyhydroxide) so far known, α-FeOOH, β-FeOOH, and γ-FeOOH occur naturally as minerals and as the corrosion products of iron. Each iron(III) oxide hydroxide exhibits characteristic properties, on which the authors have examined in several cases, such as the effect of Cu(II) on the crystal formation,[1–3] the activity to sulfur dioxide,[4] and the electrical conductivity.[5]

A study on the interaction between water molecules and iron(III) oxide hydroxide crystals is expected to clarify the corrosion process of iron surface in the atmospheric environments, since iron(III) oxide hydroxides are the main components in corrosion products. The dielectric measurement is used for the study of water adsorption because of the large dipole moment of the water molecule. Many dielectric studies on the water adsorption onto solids have been attempted. McCafferty *et al.*[6] reported the dielectric behavior of adsorbed water on α-Fe_2O_3. The correlation between the change in capacitance caused by applying electric field and the amount of adsorbed water appears significant to discuss the adsorption mechanism based on a structural view-point, because polar molecules adsorbed in a monolayer are too tightly connected with surface so as to orientate, whereas the molecules adsorbed in the second or higher layers are relatively free to orientate under the influence of the applied field.[7,8]

In this paper, the relationship between the dielectric behavior of water adsorbed on iron(III) oxide hydroxides and the surface structure of the oxyhydroxides is examined.

Experimental

Sample. Both α-FeOOH and β-FeOOH were synthesized by the methods described.[5] γ-FeOOH was prepared by the following procedure. After 3.6 g of $FeSO_4 \cdot 7H_2O$ was dissolved in 600 ml of oxygen-free water, air was blown for 3 hr into the solution adjusted to pH 4.3—6.5 with 10% NH_4OH solution. γ-FeOOH suspension thus obtained was aged at 30 °C for 5 days at pH 4.5. The crystals were filtered, washed with 2.5 l distilled water, and dried at 60 °C for 9 hr.

Examination of Samples. The X-ray diffraction patterns were obtained by the powder method with an automatic diffractometer (Geigerflex 2001, Rigaku Denki Co.) by use of Mn-filtered Fe*K*α at 30 kV and 10 mA. Electron-microscopic observations were carried out by JEM 50B (Japan Electron Optics Co.). The predominant face of α-FeOOH crystals was identified by the selected-area electron diffraction with Hitachi HU-11D. The BET surface-area was determined by Shibata surface-area meter using N_2 adsorption at liquid nitrogen temperature for the samples dried at 110 °C for 1 hr in a stream of nitrogen.

The iron content in β-FeOOH crystals was determined, after the sample had been dissolved in hydrochloric acid by titration with 0.1 M $K_2Cr_2O_7$ standard solution, and the chlorine content in β-FeOOH by the Volhard method with 0.1 M $AgNO_3$ standard solution.

Adsorption of Water. The adsorption of water vapor was measured at 30.0 °C with a conventional volumetric apparatus. The water vapor was produced from $BaCl_2 \cdot 2H_2O$. Samples were outgassed at 110 °C under 10^{-5} Torr for 15 hr prior to the adsorption measurement. The adsorption reached an equilibrium within 1 hr.

Dielectric Measurements. The dielectric constant was measured in the frequency range 200 Hz—100 kHz by a substitution-type Schering bridge. The resistance-ratio bridge used consists of a precise variable air-capacitor (Yokogawa Hewlett-Packard Co., CDS-500), a low frequency oscillator and an oscilloscope in connection with a pre-amplifier as the detector. The sample cell is made of brass coaxial cylinders 5 cm long and 2 mm apart, insulated mutually by Teflon. This cell is fitted into the annular glass receptacle which can be connected with the above-mentioned adsorption apparatus. The capacitance of the cell C_0, a constant capacitance C' in parallel with C_0, and the accuracy of the apparatus, were determined and checked by the measurements with air, benzene, cyclohexane, and dichloroethane. These solvents were dried with Na wires and distilled just before the measurements. The values of C_0 and C' were 17.0 and 10.1 pF, respectively. The accuracy of the capacitance determination was ±1% in the range 40—200 pF; the capacitance was determined mostly in this range. The apparent dielectric constant is given by $(C—C')/C_0$, where C is the capacitance of the cell filled with the water-adsorbed sample.

Results

Properties of Samples. Each sample prepared gave X-ray diffraction patterns of well crystallized

Table 1. Properties of samples

	α-FeOOH	β-FeOOH	γ-FeOOH
Crystallite size by X-ray (Å)	280	550	110
Crystal length by EM (Å)	3000	2600	900
Crystal shape	Thin rectangular plate	Long square rod	Very thin rectangular plate
Predominant face	(100)	(100), (110) or (310)[9]	(010)[10]
S_{N_2} (m²/g)	64	30	100

α-, β-, and γ-FeOOH, respectively. Table 1 gives the crystallite size calculated by the Scherrer formula from the half-value width of the principal X-ray diffraction lines, the mean crystal length by the electron microscopy (EM), the shape of crystals, and the predominant face of crystals. The predominant face of β-FeOOH crystals is cited from Mackay's results[9] and that of γ-FeOOH crystals from Oosterhout's results.[10] The specific surface area S_{N_2} by the adsorption of nitrogen is also given in Table 1. The ratio of chlorine to iron for β-FeOOH was found to be 8.2 atomic %.

Adsorption Isotherms. The adsorption isotherms at 30.0 °C for each sample are shown in Fig. 1, and are the BET II type. The monolayer-adsorption volume was determined by use of the BET plot of the adsorption data. Table 2 gives the monolayer volume V_m in milliliter of water per gram of the oxyhydroxide, the monolayer volume A_m in milliliter per S_{N_2}, and the area occupied by an adsorbed water molecule σ_w.

Dielectric Properties. Figure 2 shows the variations of apparent dielectric constant with frequency at different degrees of water adsorption for β-FeOOH. The dielectric constant of the dry sample did not exhibit any recognizable dispersion with respect to

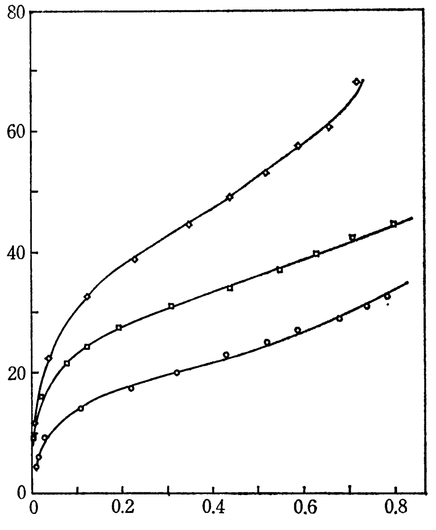

Fig. 1. Adsorption isotherms of water on α-FeOOH (□), β-FeOOH (○), and γ-FeOOH (◇).

Table 2. Monolayer volume and σ_w

	V_m (ml/g)	A_m (ml/m²)	σ_w (Å²)
α-FeOOH	24	0.37	10
β-FeOOH	12	0.38	9.7
γ-FeOOH	32	0.32	12

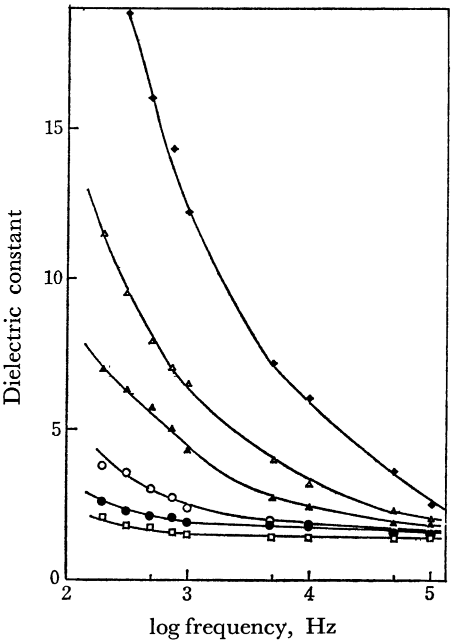

Fig. 2. Variations of dielectric constant with frequency at different degrees of water adsorption for β-FeOOH. The relative pressures are 0 for (□), 0.034 for (●), 0.067 for (○), 0.163 for (▲), 0.288 for (△), and 0.583 for (◆).

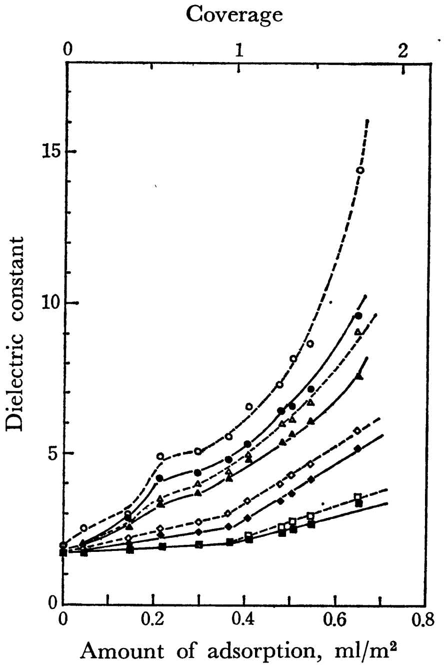

Fig. 3. Variations of dielectric constant with the amount of adsorption at various frequencies for α-FeOOH. ○: 200 Hz, ●: 500 Hz, △: 700 Hz, ▲: 1 kHz, ◇: 5 kHz, ◆: 10 kHz, □: 50 kHz, ■: 100 kHz.

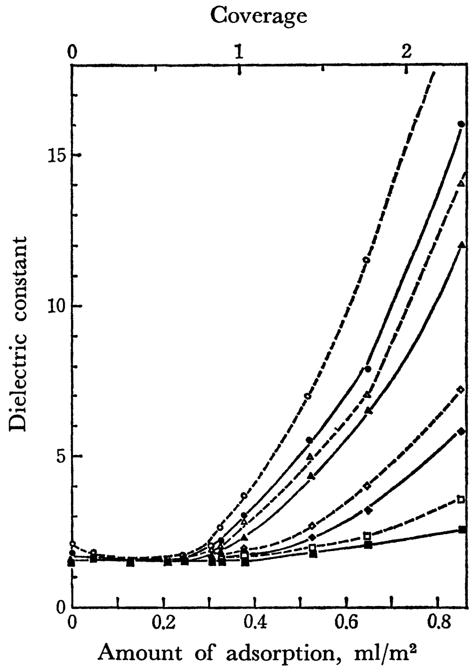

Fig. 4. Variations of dielectric constant with the amount of adsorption at various frequencies for β-FeOOH. Each symbol denotes the same frequency as that used in Fig. 3.

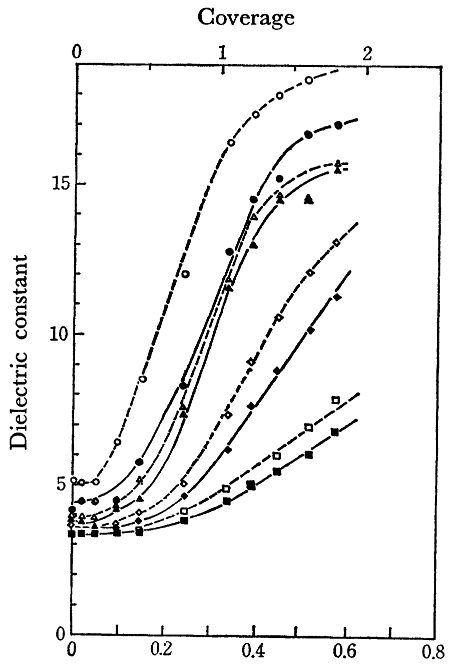

Fig. 5. Variations of dielectric constant with the amount of adsorption at various frequencies for γ-FeOOH. Each symbol denotes the same frequency as that used in Fig. 3.

frequency. The dielectric constant in lower frequency range increased considerably with the amount of adsorption, whereas that in higher frequency range increased only slightly. In Figs. 3—5, the relationship between the dielectric constant and the amount of adsorbed water in milliliter per S_{N_2} is presented at different frequencies for α-, β-, and γ-FeOOH, respectively. The coverage which indicates the number of layers of adsorbed molecules is also shown on the top abscissa of the figures. The curve at lower frequencies for α-FeOOH (Fig. 3) has a shoulder in the neighborhood of 0.6 coverage and rises steeply with adsorption at the coverage over unity. Figure 3 illustrates the fact that the dielectric constant at higher frequencies (5—100 kHz) increases with adsorption linearly and that each linear relation has a clear bend at unity of the coverage. The dielectric constant for β-FeOOH (Fig. 4) does not vary with adsorption up to 0.7 coverage (adsorbed water 0.25 ml/m²) irrespective of frequency, but it increases remarkably with adsorption above 0.7 coverage. No change in dielectric constant with the adsorption for γ-FeOOH (Fig. 5) is noticeable up to 0.5 coverage. The dielectric constant at lower frequencies with adsorption rises remarkably in the 0.5—1 range of coverage, but it increases only slightly with adsorption over unity. On the other hand, the dielectric constant at higher frequencies increases linearly with adsorption above 0.8 coverage though only slightly.

Discussion

Frequency Dependence. The dispersion of dielectric constant with frequency for the solid with adsorbed water has been explained both by the heterogeneous sturcture of the system consisting of adsorbed film, solid, and intergranular gap,[11] and by the orientation of adsorbed water under the influence of electrical field.[8] In the case of the solid with monolayer or bilayer adsorption film as in the present experiment, the dc conductance in the adsorbed film is not influenced by the dissolution of surface ions into the water film, but by the hopping of the protons in the absorbed water molecules on the solid surface. The dispersion by the latter influence may be regarded as an orientation mechanism, since the hopping of protons causes a variation in the direction of the dipole moment.

Thus the dielectric dispersion observed in the low frequency range seems to be ascribed to the transition between some different orientational directions of the dipole of adsorbed water. It is anticipated that the adsorbed water forms a structure analogous to that of ice which shows the low frequency dielectric dispersion explained by the molecular reorientaiton.[12,13] The transition of molecular orientation depends on the force on the solid surface. The low frequency dielectric constant shows sensitively the adsorption state of water molecules. On the other hand, the dielectric constant in the high frequency range, where the dipole lags behind the field, depends to a lesser extent on the adsorption state.

Dielectric Behavior and Surface Structure. Electron microscopic observation showed that the predominant face of crystals occupies more than 90% of the total surface (Table 1). The adsorption occurs therefore mainly on the predominant surfaces of each crystal. The surface structures of α-, β-, and γ-FeOOH shown in Figs. 6, 7, and 8, respectively, were illustrated from available crystallographic data (α-FeOOH,[14,15] β-

Table 3. Data on the two-dimensional unit cell of the predominant face

	Area of *TD*-unit s_u, (Å^2)	Number of H_2O per s_u, n_w	Number of OH per s_u, n_{OH}
α-FeOOH	30.3	3	2
β-FeOOH	31.7	3	2
γ-FeOOH	11.8	1	1

FeOOH,[9,16,17] and γ-FeOOH[18]). The ionic radius values of 1.40 and 1.53 Å were employed for oxygen and hydroxyl ions, respectively, in the drawing of Figs. 6—8.[19] Table 3 gives the area of the two-dimensional unit cell (TD-unit) s_u calculated from the lattice constant, the number of hydroxyls n_{OH} per s_u estimated from the structure of the predominant surfaces, and the number of water molecules n_w in the monolayer per s_u. n_w is the integer nearest to the ratio of s_u to σ_w. It is assumed that adsorption sites on α- and γ-FeOOH crystals are hydroxyls, whereas those on β-FeOOH are hydroxyls and tunnels. The dissociative adsorption of water may be ignored, since it was demonstrated that the heat of immersion in water for α- and γ-FeOOH is much less than that for α-Fe_2O_3, immersion of which in water is apparently accompanied by rehydration.[20]

The dielectric behavior of α-FeOOH with respect to the amount of adsorbed water may be explained by assuming the presence of two kinds of hydroxyl (hydroxyl-I and II) on the surface ($n_{OH}=2$). A water molecule denoted by W(I) is localized on hydroxyl-I by the triple hydrogen bonding with one OH^- and with the nearest two O^{2-}. Another water molecule W(II) is adsorbed on hydroxyl-II by the single hydrogen bond. A third water molecule W(III) assumes a position between W(I) and W(II). Figure 6 shows the state of water adsorption, where n_w equals 3. The immobile water molecules W(I) result in a slight increase in the dielectric constant up to 0.3 coverage. The freely orientating molecules W(II) exhibit a considerable increase in the dielectric constant in the 0.3—0.6 coverage range. W(III) molecules hinder the orientation of W(II); W(III) brings about a further slight increase in the dielectric constant in the 0.6—1 coverage range. Molecules in the second adsorption layer with greater freedom of movement cause a considerable increase in dielectric constant at lower frequencies.

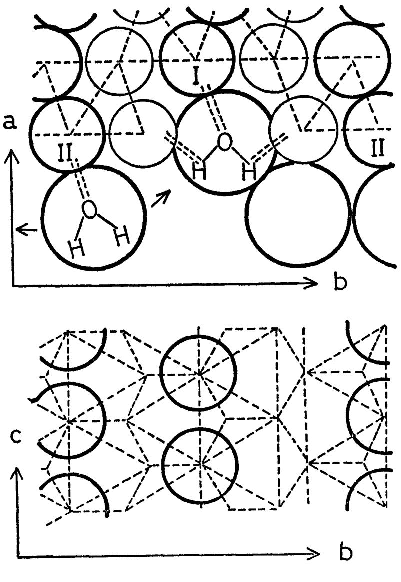

Fig. 6. Adsorption process of water molecules on the (100) plane of α-FeOOH. The smallest circle, the intermediate circle, and the largest circle denote oxygen ion, hydroxyl ion, and water molecule, respectively. The single broken line denotes the edge of the octahedron including an iron ion. The double broken line denotes hydrogen bond binding the adsorbed water molecule.

β-FeOOH is stable in the presence of F or Cl ions.[9] The Cl content in β-FeOOH can not be easily reduced below 12% by washing.[21] Mackay[9] reported that β-FeOOH has a hollandite ($BaMn_8O_{16}$) structure having tunnels parallel to the c-axis, in which Cl^- and H_2O can be occluded (Fig. 7); the extra negative charge due to Cl^- in β-FeOOH crystals must be compensated by the replacement of O^{2-} by OH^-. According to the results by Byström and Byström,[22] it is considered that in the case of hollandite a half the volume of tunnels is filled with Ba ions and the other half with water molecules; the ratio of Ba to Mn is 1/8, *viz.*, 12.5%. The chlorine in β-FeOOH plays the role of Ba ion in hollandite. The most stable composition of β-FeOOH is assumed to be $FeO_{1-1/8}(OH)_{1+1/8}Cl(t)_{1/8}H_2O(t)_{1/8}$, where (t) indicates the state bound to the tunnel. The electron-micrographs of β-FeOOH crystals obtained by several authors[9,16,23] clearly show the presence of holes, indicating that the tunnels are broken up midway. Cl ions in the neighborhood of the exits of tunnels and holes are supposedly replaced by water molecules in the course of washing. The washing process may be expressed as follows.

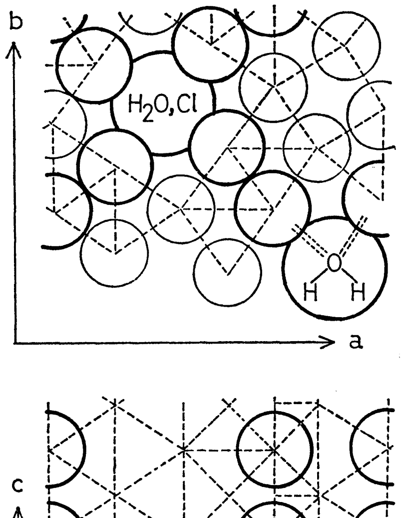

Fig. 7. Adsorption process of water molecules in the tunnels and on the cracked tunnels of β-FeOOH.

$FeO_{1-1/8}(OH)_{1+1/8}Cl(t)_{1/8}H_2O(t)_{1/8} \rightarrow FeO_{1-1/8+x}(OH)_{1+1/8-x}Cl(t)_{1/8-x}H_2O(t)_{1/8+x}$, where $1/8-x$ is equal to 8.2%. Accordingly x is equal to 4.3%. The replaced water xH_2O could be removed in the course of pretreatment. The 4.3% vacant sites thus produced can be used as the adsorption sites for water. The possible amount of water adsorbed to these sites is calculated to be 0.25 ml/m^2. Assuming that this amount of water is bound tightly in the tunnel, the fact that the dielectric constant is almost constant up to 0.25 ml/m^2 of adsorption (Fig. 4) is quite conceivable. After the tunnel is choked up, approximately 0.11 ml/m^2 water molecules are bound to the two hydroxyls at outer surfaces by the bifurcated hydrogen bonding (Fig. 7). The second step of adsorption corresponds to a slight increase in the dielectric constant in the range of the amount of adsorption from 0.25 to 0.4 ml/m^2 (A_m) (Fig. 4). The water molecules in the second layer are bound to the surface by weak forces and are mobile to orientate, when the dielectric constant increases markedly.

The dielectric behavior of γ-FeOOH with respect to the amount of adsorbed water may be explained by assuming the presence of only a kind of hydroxyl on the surface ($n_{OH}=1$). It is supposed that each water molecule is localized on two hydroxyls by the bifurcated hydrogen bonding up to the half coverage adsorption, so that only a slight increase in dielectric constant is observed in the region of coverage up to 0.5 (Fig. 5). Water molecules loosely bound to hydroxyls by single hydrogen bonds ($n_{OH}=n_w$) above the half coverage are relatively free to orientate, when the dielectric constant increases sharply. Figure 8 shows the adsorption process of water on γ-FeOOH. From the fact that the calculated density of hydroxyls on γ-FeOOH is the highest (8.4×10^{14} cm^{-2}) in comparison with 6.6×10^{14} cm^{-2} on α-FeOOH and 6.3×10^{14} cm^{-2} on β-FeOOH, it follows that even the second layer of the adsorbed water on γ-FeOOH will be comparatively ordered. The ordered adsorbed water molecule in the second layer withholds the dielectric constant from an abrupt increase in the range of coverage over unity as shown in Fig. 5.

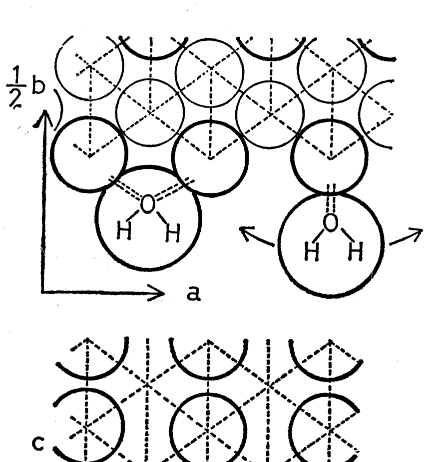

Fig. 8. Adsorption process of water molecules on the (010) plane of γ-FeOOH.

The increase in dielectric constant in a higher frequency range is due to the change in the atomic polarization, which depends on the product of the atomic polarizability and the number of molecules of adsorbed water. The atomic polarizability of the water molecule in the adsorption layer is identical, so that the dielectric constant in a higher frequency range is proportional to the number of water molecules. Therefore, the dielectric constant in higher frequency range increases linearly with the amount of adsorption. The variation in the slope of linear plots in the contiguity of monolayer capacity seems to be caused by the difference between the atomic polarizability of adsorbed water in the first layer and that in the second layer.

Conclusion

The adsorption isotherm of water on iron(III) oxide hydroxides (α-, β-, and γ-FeOOH) was found to be of the BET II type. The change in dielectric constant with the amount of adsorption of water was measured. The adsorption mechanism was discussed on a structural view-point that the relationship between the dielectric constant and the amount of adsorbed water reflects the adsorption process of coverage below unity. The structure of the predominant surface of crystals, in particular the number and position of hydroxyls, is the main determining factor in the adsorption of water; two kinds of hydroxyl on (100) plane for α-FeOOH crystal, the tunnels parallel to the c-axis and the hydroxyls on the outer surface for β-FeOOH crystal, and a kind of hydroxyls on (010) plane for γ-FeOOH crystal are the sites of adsorption. Water molecules are adsorbed on surfaces in two or three steps, which is characteristic of the surface structure of each iron(III) oxide hydroxide.

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